

Japanese Kokai Patent Application No. Hei 6[1994]-128517

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KOKAI PATENT APPLICATION NO. HEI 6[1994]-128517

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INK AND COLORING AGENT FOR INK

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[There are no amendments to this patent.]

Abstract

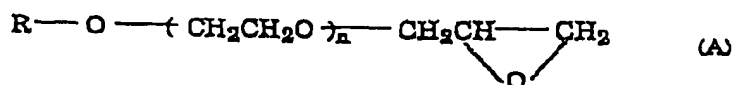
Objective

To obtain a favorable dispersibility of a carbon black in a dispersion medium and a viscosity suitable for use in an ink using the carbon black as a coloring agent.

Constitution

An ink constituted by dispersing a treated carbon black, which is obtained by reacting a carbon black at 100 parts by weight and a compound represented by general formula (A)

[Structure 1]



(Also, in the formula, R represents alkyl group, aryl group, alkylaryl group, or aryl halide group, which have $\text{C}_1\text{-C}_{30}$, and $n = 1\text{-}50$) at 5-200 parts by weight at a temperature of $50\text{-}350^\circ\text{C}$, in a dispersion medium.

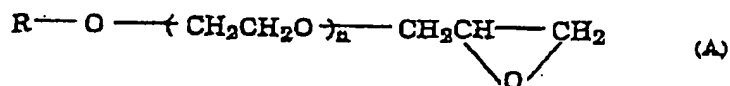
Effect

When an ink is used in writing tools, etc., since the ink discharge from the pen tip is stable and good for a long term, its writability is improved, and when the ink is used as an ink jet, the control of the ink particle diameter is easy.

Claims

1. An ink, characterized by the fact that it is constituted by dispersing a treated carbon black, which is obtained by heating and mixing a carbon black at 100 parts by weight and a compound represented by general formula (A)

[Structure 1]



(also, in the formula, R represents alkyl group, aryl group, alkylaryl group, or aryl halide group, which have $\text{C}_1\text{-C}_{30}$; $n = 1\text{-}50$) at 5-200 parts by weight at a temperature of 50-350°C, in a dispersion medium.

2. The ink of Claim 1, wherein the number-average molecular weight of the compound represented by the general formula (A) is 150-2000.

3. The ink of either Claim 1 or 2, wherein the ratio of the number C_m of carbon and the total number n of ethylene oxide units in the general formula (A) satisfies $0.02 < \text{C}_m/n < 5$.

4. The ink of any of Claims 1-4, wherein the treated carbon black is included at 1-50 wt% of the ink composition.

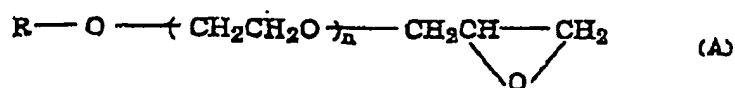
5. The ink of any of Claims 1-4, wherein the dispersion medium is a water-soluble organic solvent or a mixed solution of water and water-soluble organic solvent.

6. The ink of any of Claims 1-4, wherein the dispersion medium is water.

7. The ink of any of Claims 1-5, wherein the treated carbon black is obtained by making a water-soluble high-molecular substance exist in addition to the carbon black and the compound represented by general formula (A) and heating and mixing them.

8. A coloring agent for an ink, characterized by the fact that it is constituted by a treated carbon black obtained by heating and mixing a carbon black at 100 parts by weight and a compound represented by general formula (A)

[Structure 2]



(also, in the formula, R represents alkyl group, aryl group, alkylaryl group, or aryl halide group, which have $\text{C}_1\text{-C}_{30}$; $n = 1\text{-}50$) at 5-200 parts by weight at a temperature of 50-350°C.

9. The coloring agent for an ink of Claim 8, wherein the treated carbon black is obtained by making a water-soluble high-molecular substance exist in addition to the carbon black and the compound represented by general formula (A) and heating and mixing them.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to an ink used for writing, stamping, printing, ink jet, recorder, etc., and a coloring agent for an ink. More specifically, the present invention pertains to an ink, in which a carbon black is uniformly dispersed and which has an appropriate viscosity and a favorable writability, and a coloring agent for an ink, which has favorable dispersibility in a dispersion medium and can provide an appropriate viscosity when it is dispersed in the dispersion medium.

[0002]

Prior art

Carbon black is broadly used as a black coloring agent in the ink and paint fields, and the ink using such a carbon black exhibits favorable characteristics such as water resistance and stability over time. However, since the carbon black had a weak affinity for other substances such as organic high-molecular substances, water, and organic solvent, compared with the cohesive force between particles, it was generally necessary to disentangle the structure or secondary cohesion of the carbon black with the consumption of enormous energy using a kneading disperser such as a roll mill or ball mill in order to uniformly finely disperse the carbon black in an ink or paint. Furthermore, it was usual to use a dispersant such as surfactant and water-soluble polymer to assist the dispersion and prevent the sedimentation or cohesion during the storage as an ink or paint; however, even if the method was used, the dispersibility could be sufficiently met. Furthermore, the dispersant used tended to lower the performances of the ink or paint.

[0003]

In order to overcome such disadvantages, for example, as presented in Japanese Kokoku Patent Nos. Sho 42[1967]-22047, Sho 44[1969]-3826, and Sho 45[1970]-17284, U.S. Patent No. 3,557,040, etc., it is proposed that a carbon black graft polymer obtained by polymerizing a polymerizable monomer in the copresence of a carbon black be used. According to such a method,

since the hydrophilicity and/or the lipophilicity of the carbon black graft polymer obtained by appropriately selecting the kind of polymerizable monomer can be appropriately changed, it can be expected that the dispersibility in water or an organic solvent can be improved. However, the yield of the carbon black graft polymer obtained by the method presented in the above-mentioned literature was as low as several to tens of several %, and it existed mostly in a vinyl group homopolymer. Also, the surface treatment efficiency of the carbon black was very poor, the affinity with other substances was not improved as expected, and the dispersion state depended on the mixture or dispersion conditions in many cases.

[0004]

Furthermore, in Japanese Kokai Patent Application Nos. Sho 63[1988]-265913 and Hei 1[1989]-79278, it is shown that a carbon black graft polymer is obtained by reacting a carbon black and a polymer having a reactivity with the carbon black under specific conditions. The carbon black graft polymer obtained in this manner exhibited sufficient affinity with water or organic solvent and excellent dispersibility in these media. However, the dispersed solution could be appropriately used as a pigment paste for a chemical toning such as ink, paint, and plastic, and when the dispersed solution itself was used as an ink, in particular, an aqueous ink, the ink viscosity was increased too high. When the dispersed solution was used in writing tools, etc., the ink discharge from the pen was slow, or ink blot, ink bleeding, or bleeding through occurred often, and when it was used for an ink jet, the ink particle diameter could not be controlled.

[0005]

Problems to be solved by the invention

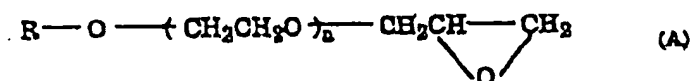
Therefore, the purpose of the present invention is to provide a new ink for use in writing tools, stamps, printing, ink jets, recorders, etc. Another purpose of the present invention is to provide an ink which includes a carbon black as a coloring agent and has a viscosity suitable for its use and in which the carbon black is uniformly finely dispersed in a dispersion medium. Furthermore, another purpose of the present invention is to provide a coloring agent for an ink which improves dispersibility of a carbon black in a dispersion medium and has favorable viscosity characteristic.

[0006]

Means to solve the problems

The above-mentioned purposes are achieved by a coloring agent for an ink which is constituted by dispersing a treated carbon black obtained by heating and mixing a carbon black at 100 parts by weight and a compound represented by general formula (A)

[Structure 3]



[0008]

(Also, in the formula, R represents alkyl group, aryl group, alkylaryl group, or aryl halide group, which have C_1-C_{30} , and $n = 1-50$) at 5-200 parts by weight at a temperature of 50-350°C in a dispersion medium, and an ink constituted by dispersing the coloring agent for an ink in the dispersion medium.

[0009]

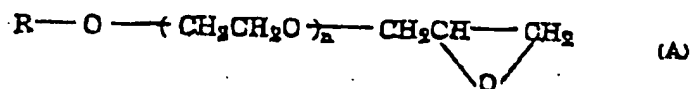
The carbon black used in the present invention may have a carboxyl group and/or a hydroxy group as a functional group on its surface. For example, any of furnace black, channel black, acetylene black, lampblack, etc., can be used, and ordinary products on the market can be used as they are. However, considering the reactivity with an epoxy group which is a terminal reactive group of the compound represented by general formula (A), carbon black with a pH of 8 or less, preferably 6 or less is preferable. The reason for this is that if pH of the carbon black is too high, the reactivity with the epoxy group is lowered. Also, a testing method of pH of the carbon black is based on JIS K 6211.

[0010]

On the other hand, a compound being grafted with such a carbon black is represented by general formula (A).

[0011]

[Structure 4]



[0012]

Also, in general formula (A), R represents alkyl group, aryl group, alkylaryl group, or aryl halide group, which have $\text{C}_1\text{-C}_{30}$, and among them, a straight-chain or branched-chain alkyl group of $\text{C}_6\text{-C}_{20}$ such as dodecyl and tridecyl, aryl group such as phenyl and naphthyl, alkylaryl group of $\text{C}_4\text{-C}_{20}$ such as p-dodecylphenyl and p-tert-butylphenyl, and aryl halide group having 1-4 halogen substituents such as chlorophenyl, dichlorophenyl, bromophenyl, dibromophenyl, and bromochlorophenyl are preferable. A straight-chain or branched-chain alkyl group of $\text{C}_6\text{-C}_{20}$ is more preferable. Also, in general formula (A), the repetitive number n of ethylene oxide $(-\text{CH}_2\text{CH}_2\text{O}-)$ is 1-50, more preferably 5-30. Furthermore, the ratio of the number C_m of carbon and the total number n of ethylene oxide molecules in general formula (A) is preferably $0.02 < \text{C}_m/n < 5$, more preferably $0.2 < \text{C}_m/n < 3$. In other words, if C_m/n is less than 0.02, the water resistance of the ink of the present invention is not likely to be sufficient, while if C_m/n is more than 5, the dispersibility of the treated carbon black obtained is quite likely to be lowered. Furthermore, the number-average molecular weight of the polymer represented by general formula (A) is about 150-2000, more preferably about 300-1500. That is, if the number-average molecular weight of the

polymer represented by general formula (A) is less than 150; the dispersibility of the carbon black cannot be sufficiently improved, even by grafting such a polymer. On the other hand, if the number-average molecular weight is more than 2000, the viscosity of the ink of the present invention is increased, so that the ink is not likely to be suitable for writing tools, stamps, printing, ink jets, recorders, etc.

[0013]

As the polymer represented by general formula (A), specifically, for example, lauryl alcohol (ethylene oxide), glycidyl ether, phenol (ethylene oxide), glycidyl ether, etc., are preferably mentioned.

[0014]

The coloring agent for an ink of the present invention is composed of a treated carbon black obtained by heating and mixing the above-mentioned compound represented by general formula (A) at a temperature of 50-350°C, preferably 100-200°C with the carbon black. If the treatment temperature is higher than 350°C, the compound represented by general formula (A) is very likely to be changed in quality. On the other hand, if the treatment temperature is lower than 50°C, a sufficient reaction cannot be generated, and the graft rate of said compound to the carbon black is lowered, so that the cohesion of the carbon black cannot be improved.

[0015]

Furthermore, in the coloring agent for an ink of the present invention, the ratio of the carbon black and the compound represented by general formula (A) is the compound represented by the general formula at 5-200 parts by weight to the carbon black at 100 parts by weight. In other words, if the compound represented by general formula (A) is less than 5 parts by weight to the carbon black at 100 parts by weight, when said treated carbon black is dispersed in a dispersion medium, the dispersibility is insufficient. On the other hand, if the compound is more than 200 parts by weight, when the carbon black in the ink is set to an optimal amount, the viscosity of the obtained ink is raised, so that the versatility is inferior.

[0016]

Also, in the reaction, stirring and mixing are preferably carried out, so that when the carbon black in a secondary cohered state used as a raw material is stirred, mixed, and reacted, it is crushed with favorable efficiency. Thereby, a fine and uniform particle diameter is obtained, and the efficiency of the reaction is also improved. Thus, the characteristics of the treated carbon black obtained are much more raised. Furthermore, the stirring and mixing are preferably carried out when the carbon black and the polymer represented by the general formula (A) have a torque value of 0.1-20 kg·m, preferably 0.3-10 kg·m.

[0017]

In the manufacture of the treated carbon black being the coloring agent for an ink of the present invention, the heating and mixing for causing the reaction of the carbon black and the compound represented by general formula (A) may be carried out by a method for heating and mixing only these two components or a method for heating and mixing them in the copresence of other substances such as polymers, polymerizable monomers, organic solvents, and water other than the compound represented by general formula (A). However, considering the smooth treatment and the viscosity of the ink obtained, the method for heating and mixing them in the copresence of a water-soluble high-molecular substance other than the compound represented by general formula (A) is preferable. As such a water-soluble high-molecular substance, for example, nonionic surfactants such as polyethylene glycol, polypropylene glycol, polyvinyl alcohol, polyoxyalkyl phenol ether, and polyoxyethylene fatty ester and anionic surfactants such as sodium salt of formaldehyde β -naphthalenesulfonate condensed product and sodium ligninsulfonate are mentioned; however, the polyethylene glycol is most preferable in terms of a combination effect with the compound represented by general formula (A). Also, the molecular weight of these water-soluble high-molecular substances is preferably 150-10,000, more preferably 150-1000. As a specific example showing the embodiment of the method for manufacturing the treated carbon black included in the ink of the present invention, for example, the polymer represented by general formula (A) at 5-200 parts by weight, preferably 10-100 parts by weight and a mixture of water-soluble high-molecular substance at

0-200 parts by weight, preferably 5-200 parts by weight, polymerizable monomer at 0-200 parts by weight, and organic solvent or water at 0-200 parts by weight are stirred and mixed at a temperature of 50-350°C to the carbon black at 100 parts by weight.

[0018]

Since the treated carbon black obtained in this manner is constituted by the reaction of the carbon black and the compound represented by the above-mentioned general formula (A), and the epoxy group, which is a reactive group of said compound, has a high reactivity with the functional group of the surface of the carbon black, the component of said compound is grafted with the carbon black surface with high efficiency. For this reason, in the treated carbon black obtained, the affinity with various substances is improved, and for example, the dispersibility in organic high-molecular substances, water, organic solvents, etc., is excellent. In particular, the dispersibility in water is remarkably excellent. When the treated carbon black is dispersed in various kinds of dispersion media to provide favorable lubrication, an appropriate viscosity is displayed, and it can be appropriate for use as a coloring agent for an ink, in particular, a water-soluble ink. The dispersion of the treated carbon black into a dispersion medium is very easy, and it is not necessary to apply a high shear stress for dispersion. The treated carbon black and water and/or an organic solvent can be dispersed at standard temperature or heated temperature into a dispersion medium, simply by stirring them using a stirrer with a propeller blade or horizontal blade, for instance. Also, the

carbon black and the compound represented by general formula (A) are heated and mixed in the presence of water and/or an organic solvent; since the treated carbon black is obtained as a dispersed solution, it can be used as it is as an ink, and if necessary, the amount of treated carbon black mixed into a dispersion medium can also be adjusted.

[0019]

The ink of the present invention is constituted by dispersing the treated carbon black, which is obtained by reacting the carbon black with the compound represented by the above-mentioned general formula (A) as mentioned above, in a dispersion medium, and the amount of treated carbon black mixed in the dispersion medium also depends on the kind of dispersion medium being used. However, the treated carbon black is included at preferably 1-50 wt%, more preferably 3-30 wt% of the ink composition to obtain a favorable writability and to obtain a favorable ink discharge for a long term without causing ink bleeding or bleeding through.

[0020]

As the dispersion medium used in the ink of the present invention, water, organic solvent, or a mixed solution of water and organic solvent can be used. However, among them, water; glycol solvents such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, and 1,8-butylene glycol; glycol ether solvents such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and ethylene glycol monobutyl

ether; glycol ether ester solvents such as ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate; pyrrolidone solvents such as glycerin, 2-pyrrolidone, and N-methyl-2-pyrrolidone; alcohol amine solvents such as triethanolamine, diethanolamine, and monoethanolamine; water-soluble organic solvents such as sulfolane, or a mixed solution of water and these water-soluble organic solvents are preferable. In particular, water and a mixed solution of water and water-soluble organic solvents is preferable. When the above-mentioned water-soluble organic solvent is used as a dispersion medium by adding water, since the water-soluble organic solvent functions as an evaporation suppressor, the improvement of storage and nonvolatilization of the ink with time can be expected. Also, the addition ratio of the water-soluble organic solvent to water depends on the kind of water-soluble organic solvent; however, it is preferable to use the water-soluble organic solvent at 70 parts by weight or less, preferably 5-60 parts by weight to the water at 100 parts by weight. In other words, if the water-soluble organic solvent is mixed at more than 100[sic; 70] parts by weight to the water at 100 parts by weight, the viscosity of the obtained ink is raised, so that the ink discharge is deteriorated, or ink bleeding or bleeding through is likely to be distinct.

[0021]

Also, in the ink of the present invention, in addition to the above-mentioned treated carbon black and dispersion medium, if necessary, various kinds of well-known additives can be further added. As the additives, for example, nonionic

surfactants such as polyethylene glycol, polyoxyalkyl phenol ether, and polyoxyethylene fatty ester; anionic surfactants such as sodium salt of formaldehyde β -naphthalenesulfonate condensed product and sodium lignin sulfonate; lubricants such as silicone resin, phosphoric ester, fluorine surfactants, dithiophosphate, dithiocarbamate derivatives, and molybdates; antimold agents such as sodium benzoate and sodium dihydroacetate; anticorrosive agents such as dialkylthiourea, benzotriazole, or phosphoric ester; antiseptics such as phenol and 1,2-benzisothiazoline-3-one; tackifiers of sugar such as dextrin and sorbitol; pen tip antidrying agents such as urea or urea derivatives; pH adjusters such as sodium carbonate and ethanolamines, etc., are mentioned.

[0022]

Application examples

Next, the present invention is explained in further detail by the application examples; however, the present invention is not limited to the following application examples. Also, in the following examples, "parts" means parts by weight.

[0023]

Application Example 1

100 parts carbon black MA-100 (made by Mitsubishi Chemical Industries Ltd.), 25 parts Denacol[transliteration] EX-171 (made by Nagase Kasei Kogyo K.K., lauryl alcohol (ethylene oxide)₁₆

glycidyl ether), and 75 parts PEG 200 (made by Sanyo Chemical Industries, Ltd., polyethylene glycol (a degree of polymerization of 4-5)) were kneaded for 15 min under conditions of 150°C and 100 rpm using a lab blast mill (made by Toyo Seiki Co., Ltd.) and cooled, so that a treated carbon (1) was obtained.

Treated carbon (1)	10 parts
Propylene glycol	10 parts
Ethylene glycol	20 parts
Water	60 parts

Then, the treated carbon (1) obtained in this manner was mixed with a dispersion medium at the above-mentioned mixture ratio and dispersed by a stirrer, so that an aqueous ink was prepared. When the particle diameter of the carbon black in the ink obtained was measured by a centrifugal sedimentation method, it was about 0.03 μm . When it was used as an ink for an aqueous felt-tip pen, there were no problems such as scratches of writing traces even after writing 3000 characters, and the water resistance was excellent. Even after holding the ink for several months, there was no change in quality, and a favorable writability was displayed.

[0024]

Comparative Example 1

Similarly to Application Example 1 except for using 5 parts untreated carbon black MA-100 instead of 10 parts treated carbon (1), an aqueous ink was prepared. When the particle diameter of the carbon black in the ink obtained was measured by the centrifugal sedimentation method, it was about 5.0 μm . The

dispersed solution was unstable, and the carbon black that was immediately sedimented was also seen. Also, in a writing test in which the ink is used as an ink for an aqueous sign pen, scratches of writing traces were generated.

[0025]

Application Example 2

100 parts carbon black MA-100R (made by Mitsubishi Chemical Industries Ltd.), 50 parts Denacol EX-145 (made by Nagase Kasei Kogyo K.K., phenol (ethylene oxide), glycidyl ether), and 50 parts PEG 400 (made by Sanyo Chemical Industries, Ltd., polyethylene glycol (a degree of polymerization of 7-8)) were kneaded for 15 min under conditions of 160°C and 100 rpm using a laboratory blast mill (made by Toyo Seiki Co., Ltd.) and cooled, so that a treated carbon (2) was obtained.

Treated carbon (2)	21 parts
Diethylene glycol	20 parts
PEG 200	10 parts
Water	60 parts

Then, the treated carbon (1) obtained in this manner was mixed with a dispersion medium at the above-mentioned mixture ratio and dispersed by a stirrer, so that an aqueous ink was prepared. When the particle diameter of the carbon black in the ink obtained was measured by a centrifugal sedimentation method, it was about 0.02 μm . When it was used as an ink for an ink jet, a very sharp printed image without clogging and ink bleeding was obtained.

[0026]

Effect of the invention

As mentioned above, the ink of the present invention is constituted by dispersing the treated carbon black, which is obtained by heating to 50-350°C and mixing the carbon black at 100 parts by weight and the compound represented by general formula (A) at 5-200 parts by weight. In the above-mentioned treated carbon black, the polymer represented by general formula (A) is strongly coupled with favorable efficiency with the surface of the carbon black, and the surface characteristics of the carbon black are enhanced, so that the affinity to various kinds of dispersion media being used, in particular, aqueous dispersion media and a favorable lubrication are offered. Thus, the carbon black in the ink of the present invention is uniformly and microscopically dispersed, and its viscosity is appropriate. Therefore, since the ink of the present invention, in particular, the aqueous ink has no ink blot or blurring of letters or ink bleeding or bleeding through and a smooth ink is obtained for a long term, the control of the ink particle diameter is easy even when it is used for an ink jet. Furthermore, since the carbon black is used as a coloring agent, favorable water resistance, colorability, stability with water, etc., are exhibited. Thus, it is suitable for writing tools, stamps, printing, ink jets, recorders, etc. Also, since the above-mentioned treated carbon black markedly improves the disadvantage of a low dispersibility of the carbon black in a dispersion medium and also enhances the viscosity characteristic, it is appropriately provided as a coloring agent for ink.